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THE CRYSTAL GROWTH AND CHARACTERIZATION OF CeT_2Si_2 TERNARY INTERMETALLICS (T = Ni, Pd, Pt)

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Bulk single crystals of the ternary intermetallic compounds $CeNi_2Si_2$, $CePd_2Si_2$ and $CePt_2Si_2$ have been grown from the melt with a modified "tri-arc" Czochralski method. The as-grown crystals were characterized by X-ray, microprobe, and chemical analyses. The measured densities were compared with the calculated densities as obtained from the lattice parameters. In all as-grown single crystals no detectable precipitates of foreign phases were observed. These precipitates are always present in polycrystalline samples, even after a heat-treatment, and are visible on the grain boundaries and in the subgrain structure.

1. Introduction

The ternary compounds MT_2X_2, with M = RE, Th, U, T = 3d, 4d or 5d metal, and X = Si or Ge, attracted much interest because of the complex behavior of the magnetic and superconducting properties [1–4]. These compounds crystallize in two allotropic modifications of the tetragonal $BaAl_4$-type structure [5]. Most compounds were found in the body-centred tetragonal $ThCr_2Si_2$-type structure [6], and some in the primitive tetragonal $CaBe_2Ge_2$-type structure [7]. $LaIr_2Si_2$ even adopts both structures as a low-temperature and high-temperature modification, respectively [8]. For the compounds with T = Pt an even lower symmetry than the $CaBe_2Ge_2$-type structure was found, characterized by the absence of an diagonal glide plane [9].

The MT_2Si_2 compounds are formed in a strong exothermic reaction. All polycrystalline samples, mostly prepared by arc-melting and subsequent annealing procedure, are contaminated by second phases, sometimes not detectable by standard X-ray techniques. However, light microscopy and microprobe analyses can clearly indicate their presence, forming precipitates on the grain boundaries as well as in the subgrain structure. The origin of these precipitates is twofold. First, the RE, U and T elements, as well as their silicides, will always contain several percents of their oxides. Second, the accuracy is limited by weighing accuracy and melting losses. The occurrence of M-oxides leads to an excess of T-silicides which may form a three-dimensional network on the grains. As many T-silicides are superconductors, this can give rise to a superconducting network that even may shield the bulk material. Here, AC susceptibility and resistivity are not reliable and specific heat or Meissner effect measurements are required to prove bulk superconductivity. Moreover, the formation of precipitates leads to a certain periodicity in the concentration gradients from grain to grain or leads to off-stoichiometry in the vicinity of grain boundaries. Our experience is that a heat-treatment at low temperatures (below 1200°C) does not improve the quality of the polycrystalline samples, but only improves the formation of a three-dimensional network of the precipitates on the grain boundaries. When annealing at higher temperatures, a contamination of the samples by the crucible material can not be excluded, due to the high reactivity of the rare earth or uranium.

We have produced several bulk single crystals

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of these ternary compounds by means of the Czochralski method. The conditions for the bulk crystal growth of CeT_2Si_2, with T = Ni, Pd or Pt, are presented in this article. Single crystals of UT_2Si_2, with T = Ni, Ru, Pd, or Pt, $LaPd_2Si_2$ and $LuPd_2Si_2$ and $LaRh_2Si_2$ have succesfully been prepared by the same method [10].

There are three main reasons to grow bulk single crystals of these compounds. First, there are large anisotropies in the physical properties, which make an interpretation of the experimental results on polycrystalline samples difficult or even impossible, especially if preferential orientations and textures are present. Second, the neutron scattering experiments on polycrystalline samples leave many questions unanswered, e.g. the critical behavior of $CePd_2Si_2$ [11].

Finally, it is believed that formation of precipitates in the matrix during our crystal growth procedure of near-equilibrium conditions, is substantially suppressed. Here, precipitates are only deposited on the surface and not built in the crystal.

2. Crystal growth

The crystal growth of the CeT_2Si_2 compounds was performed on a modified "tri-arc" Czochralski method, as described extensively by Menovsky and Franse [12]. This equipment is now completed with a colour TV system (camera type Minicam and Hitachi CCD sensor), which is part of an automatic diameter control system [13].

Ultrapure elements in a stoichiometric ratio were arc melted in a separate furnace to yield a melt of 10–20 g. An as-cast cylinder with a diameter of 3 mm and 20 mm long served as a polycrystalline pulling tip. Bulk single crystals grew quite easily on the polycrystalline pulling tip after a few millimetres, so that no necking procedure was necessary. Weight losses during the crystal growth as well as during the arc-melting were negligible, as can be expected from the low vapour pressure of the elements at the melting temperature of the compounds. The impurities, which exist in the starting materials of Ce-oxides and/or T-silicides, formed a solid thin skin on the surface of the melt. These impurities were partially pulled out with the growth of the crystal and partially deposited on the colder part of the melt, in the vicinity of the cold crucible. The characteristics of the growth procedure are presented in table 1.

3. Results and discussion

The main motivation for this work was to prepare bulk single crystals of dimensions large enough for physical investigations, and to keep the contamination as low as possible. The "tri-arc" cold crucible technique proved to be very suitable, and no further efforts were necessary to optimize

Table 1
Characteristics of the growth of some single crystals

Compound	$CeNi_2Si_2$	$CePd_2Si_2$	$CePt_2Si_2$
Congruent melting temperature (°C)	~ 1500	~ 1500	~ 1500
Vapor pressure of elements at T_m of compound (10^{-5} Torr)	Ce $x = 3$ Ni $x = 2$ Si $x = 3$	Ce $x = 3$ Pd $x = 2$ Si $x = 3$	Ce $x = 3$ Pt $x = 6$ Si $x = 3$
After-heating	No	No	No
Getter material	Ti	Ti	Ti
Tip material	As-cast	As-cast	As-cast
Argon pressure (Torr)	900	950	900
Pulling rate (mm/h)	15	15	10
Tip rotation rate (rpm)	3–23	12	23
Hearth rotation rate (rpm)	18	18	18

the growth parameters, starting material composition and starting material purity. Our experience with the preparation of the polycrystalline samples showed that the physical–chemical properties are favourable to grow single crystals. These compounds namely have a high melting temperature, are formed by a strong exothermic reaction and form facets when cooling the melt. This facetting phenomenon was also observed when growing the single crystals, and depends closely on the growth direction. The larger facets were formed when the growth direction was closer to the *a*-axis.

The as-grown single crystals of $CeNi_2Si_2$ and $CePd_2Si_2$ are shown in fig. 1. Generally, the as-grown crystals are stable in air, very hard, and easy to cleave in the basal plane. Only $CePd_2Si_2$ had a tendency to crack. The cracks are probably due to a too high cooling rate and may be avoided by after-heating. Another possibility to avoid cracks is to change the growth direction. Moreover, a structural phase transition from a high temperature to a low temperature phase, as ob-

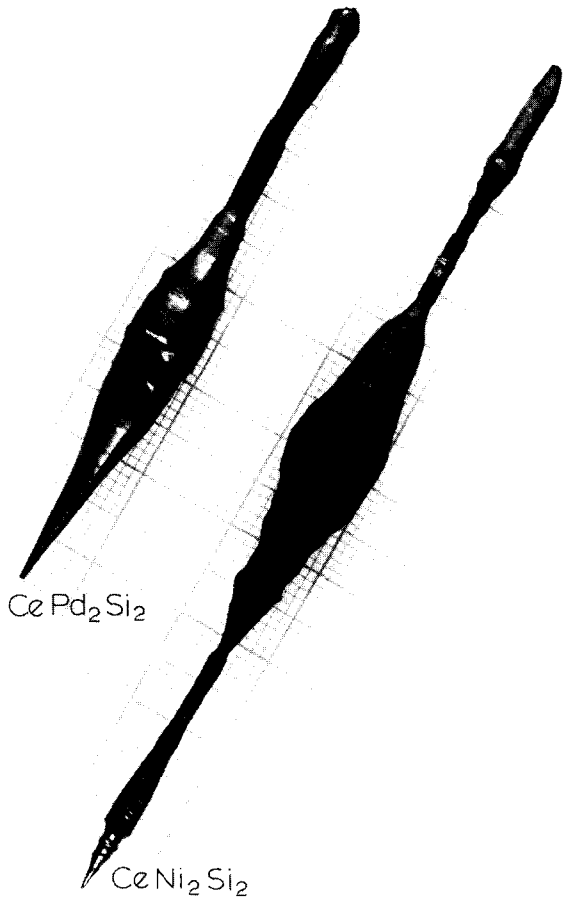

Fig. 1. As grown single crystals $CeNi_2Si_2$ and $CePd_2Si_2$.

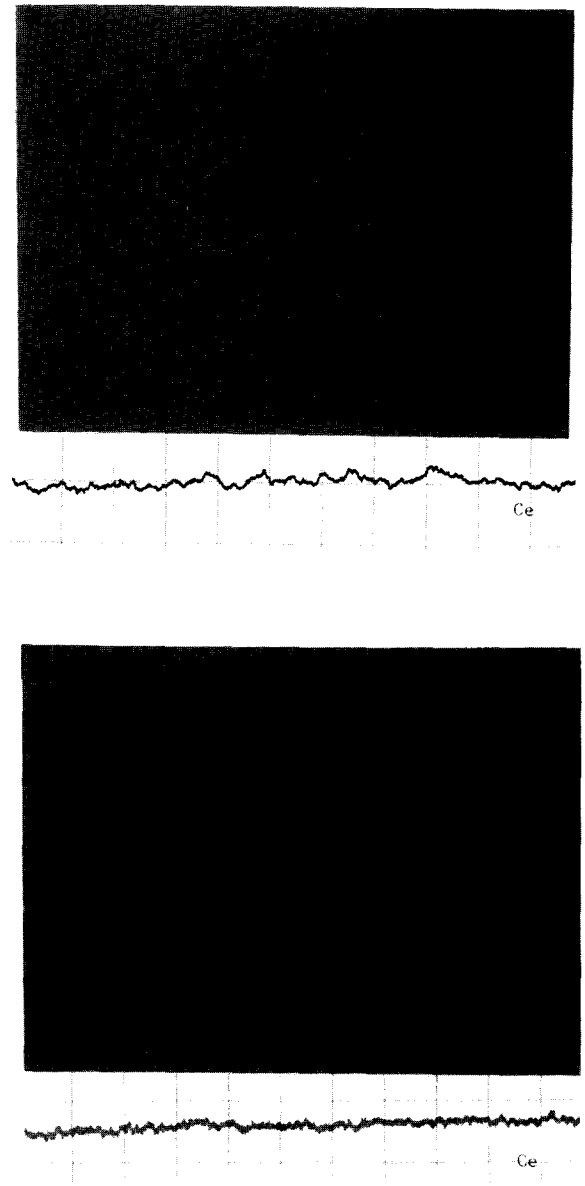

Fig. 2. A typical light micrograph of a polished (100) surface (above) and microprobe linescan of cerium (below). A linescan traject indicated: (a) $CePt_2Si_2$; (b) $CePd_2Si_2$.

served by Braun in case of $LaIr_2Si_2$ [8], cannot be excluded.

Laue pictures of the as-grown crystals were of rather poor quality, due to the presence of impurities on the surface. These impurities consisted of Ce-oxides and were the only contamination of the crystals. However, Laue pictures of cleaved or spark-cut surfaces showed single-grain patterns with very sharp spots for all single crystals. Light microscopy observations proved the single-grain structure and no foreign phases or voids were detected. Microprobe analysis on pieces cut from the top and bottom of the as-grown crystals showed an uniform composition as shown in fig. 2. The chemical analysis confirmed the stoichiometric composition of all prepared crystals.

The Debye-Scherrer patterns were indexed on basis of the tetragonal $ThCr_2Si_2$-type structure. This structure has the reflection condition $\Sigma(h, k, l) =$ even. Here, we observed a disagreement for all samples between the measured and calculated intensities. We think that this discrepancy arises from a preferential orientation in the powder, due to the easy cleavage in the basal plane. However, a random distribution of the T and Si atoms in case of $CeNi_2Si_2$ and $CePd_2Si_2$ can be excluded because of the total absence of reflections with an odd sum of Miller indices. Only for $CePt_2Si_2$ we found reflections with an odd sum of Miller indices. This means that $CePt_2Si_2$ either adopts the $CaBe_2Ge_2$-type structure, or has a random distribution of Pt and Si atoms. The Debye–Scherrer method cannot make any distinction between two possibilities, and a distinction is subject to further investigation.

Mayer and Yetor [14] also found a disagreement between the calculated and observed intensities for other MPt_2Si_2 compounds. They concluded from their calculations that the Pt and Si atoms are randomly distributed over the 4(d) and 4(e) sites. This effect was ascribed to the tetravalent character of both the Pt and Si atoms. However, these authors overlooked the possibility of the $CaBe_2Ge_2$-type structure which gives identical results. Recently, Hiebl and Rogl [9] calculated that the degree of disorder in $CePt_2Si_2$ was less than 10%, leading uniquely to the $CaBe_2Ge_2$-type crystal structure. However, these authors additionally found reflections $(h, k, 0)$ with $\Sigma(h, k) =$ odd, which are symmetry forbidden in the $CaBe_2Ge_2$-type crystal structure. This means that the symmetry lowers from P4/nmm ($CaBe_2Ge_2$, primitive tetragonal) even to P4mm ($CePt_2Si_2$), with the absence of a diagonal glide plane [9]. We cannot confirm their latter observation because the intensity of the $(h, k, 0)$ lines in the X-ray powder diffractograms is to weak with respect to our experimental resolution. The characteristic parameters are presented in table 2.

In fig. 3 we present magnetization measure-

Table 2
Structure, lattice parameters and densities of as-grown crystals

	Compound			
	$CeNi_2Si_2$	$CePd_2Si$		$CePt_2Si_2$
Type of structure	$ThCr_2Si_2$	$ThCr_2Si_2$		$CaBe_2Ge_2$
Symmetry system	Tetragonal	Tetragonal		Tetragonal
This work:				
Unit cell parameter (Å)	$a = 4.036$	$a = 4.230$		$a = 4.253$
	$c = 9.57^5$	$c = 9.873$		$c = 9.800$
Density, experimental (g/cm^3)	6.683	7.605		10.818
Density, calculated (g/cm^3)	6.678	7.688		10.983
Literature reference:	[7]	[16]	[17]	[16]
Unit cell parameter (Å)	$a = 4.027$	$a = 4.232$	$a = 4.212$	$a = 4.246$
	$c = 9.557$	$c = 9.911$	$c = 9.98$	$c = 9.837$
Density, experimental (g/cm^3)	–	–	–	–
Density, calculated (g/cm^3)	6.720	7.652	7.671	10.98

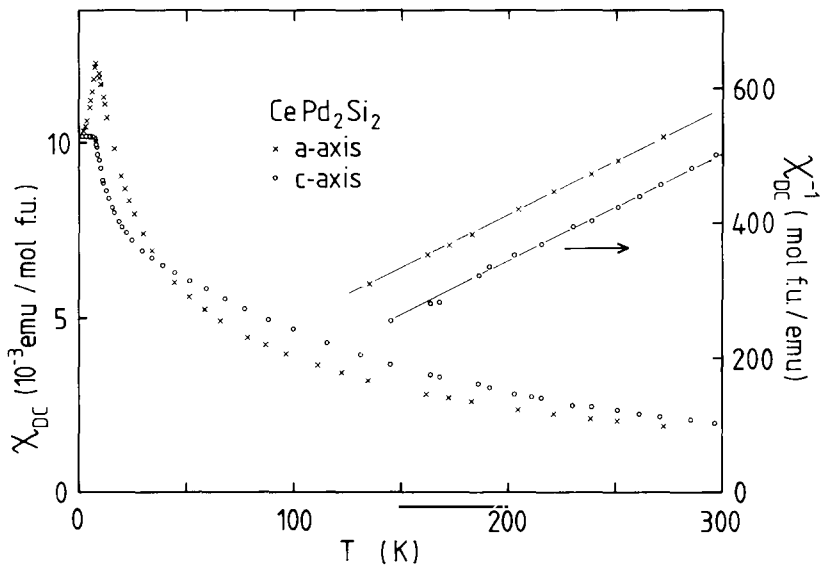

Fig. 3. DC susceptibility $\chi_{DC} \equiv M/B$ and inverse susceptibility of $CePd_2Si_2$ measured in a magnetic field of $B = 4$ T parallel to the a- and c-axes.

ments for $CePd_2Si_2$ along the a- and c-axis, to illustrate the anisotropic behavior. From these measurements it is evident that the properties are strongly anisotropic, not only in magnitude but also in character.

4. Conclusions

It is shown that the "tri-arc" Czochralski method is very suitable for the preparation of bulk single crystals of some highly reactive Ce ternary compounds. These single crystals are indespensable for the interpretation of physical measurements, due to the large anisotropy [15]. Further investigations on this crystal structure and its homogeneity range are under progress, as well as the growth of pseudo-ternary compounds of this crystal structure.

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